

# PATENT SPECIFICATION

1,099,464

DRAWINGS ATTACHED.

Inventor:—ROBERT NEVIL GARROD LINGWOOD.

Date of filing Complete Specification (under Section 3(3) of the Patents Act, 1949): Oct. 22, 1964.

Application Date: Oct. 24, 1963. No. 42028/63.

Application Date: Oct. 28, 1963. No. 42496/63.

Complete Specification Published: Jan. 17, 1968.

© Crown Copyright 1968.



1,099,464

Index at Acceptance:—C1 A(D10, G9, G13, G22, T8A) AG9D10, AG13D10, AG22D10);  
C7 D(5K6, 5L2, 5M3, 5N2, 5N5, 5N9, 8D, 8G, 8M, 8R, 8Z2,  
8Z13, 9B1A, 9B2A, 9B3A, 9B3D, 14A2, 14A3B, 14A3C, 24).

Int. Cl.:—C 21 b 1/08.

## COMPLETE SPECIFICATION.

### Composition of Matter Convertible to Stable Metallic Form by Hydrogen Reduction.

We, RESEARCH COUNCIL OF ALBERTA, a Body Corporate organised and existing under the Research Council Act of the Province of Alberta, Canada, of 87th Avenue and 114th Street, Edmonton, Alberta, Canada, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a composition of matter convertible to stable metallic form by hydrogen reduction at less than the melting temperature of the metal.

Hydrogen reduction of many metal compounds especially if conducted at temperatures less than the melting temperature of the metal produced will result in an unstable metal product. Sponge iron produced by hydrogen reduction may be pyrophoric. Cobalt or nickel sponge similarly produced exhibit unstable or pyrophoric properties derived from an undesired affinity for oxygen. The word "unstable" as used in this sense in this specification thus refers to an undesired affinity for chemical transfer or change as contrasted with stable metals of ordinary usage which though taking on oxide or other films over a period of time do not corrode or convert at such a rate as to render same impractical for industrial and commercial usage as relatively stable materials.

The hydrogen reduction of metal compounds has the problems of hydrogen recovery, reclamation and/or regeneration so that it cannot compete successfully on a large scale with the economies and efficiencies of ordinary carbon monoxide reduction.

[Price

although in many respects hydrogen is a superior reducing gas to carbon monoxide especially as to the purity of the metal produced. Metal chloride systems of various metals and especially of iron have encountered most severe problems during attempts to convert the chlorides to metal form with hot reducing gases.

A composition of matter according to this invention comprises a mixture of a compound of iron, cobalt or nickel with at least twenty per cent. by weight of the metal content in the form of a chloride of the metal. Such mixtures when reduced by hydrogen at less than melting temperature of the metal deliver a stable metal product of non-pyrophoric nature. The metal chlorides are reduced with hydrogen at high efficiencies and practical rates preferably by a three stage reduction process according to the invention involving in turn within a reducing atmosphere dehydration, reduction to sponge form at less than final reduction gas temperatures to provide a support for the mass being reduced and a third stage of higher temperature fast reduction to final metallic form.

An unexpected property has been noticed in a large number of metal products from metal chlorides, alone or with other metal compounds especially oxides, reduced with hydrogen according to the invention. For some reason which cannot be accounted for, nickel metal products exhibit a uniform sponge structure of definite physical integrity conforming to the original geometry of the shape of the mass before reduction and having a metallic ring (as close as can be des-

40

45

50

55

60

65

70

75

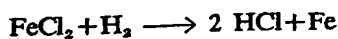
DA

cribed) when struck by another similar sample. Cobalt products on the other hand may not be said to be as uniform but nearly so and yet they seem to exhibit a different but nevertheless metallic sound. Iron products however mostly swell and distort substantially from the original geometry of the mass before reduction to the degree that in many instances the form is completely disrupted. No metallic sound can be obtained from such samples but only a brittle scraping sound. Changes in sintering control have offered no explanation for these differences in sound.

Still further and unexpected has been the quite unrelated and yet definite contribution to physical integrity of iron products to the degree that they achieve a metallic sound and maintain geometry if containing trace amounts of calcium, sodium, sulphur or vanadium.

The process of the invention generally comprises establishing as a portion of the compound prior to hydrogen reduction thereof 20 per cent by weight of the elemental content of the compound as a bivalent chloride of the metal thereby to render the reduced metallic form of metal produced more stable and essentially non pyrophoric. The compound to be reduced is generally dehydrated at less than reduction temperatures in the hydrogen atmosphere of the reduction zone if this has not happened before.

One of the difficulties encountered is the considerable endothermic heat of the reaction:



in the case of solid phase reduction. A more serious difficulty is the self-poisoning nature of the reaction: the hydrogen chloride produced prevents further reaction and promotes sublimation of the ferrous chloride unless it is efficiently removed. The difficulty is such that a bed of fine ferrous chloride powder is more likely to melt (MP. 674°C) than reduce, if hydrogen at 675°C is passed through it. This is in spite of the fact that the equilibrium constant of the reaction

$$(K_p = \frac{p^2 \text{HCl}}{p^2 \text{H}_2}) \text{ should enable the gas leaving}$$

a static bed reactor in equilibrium at 650°C to contain 14% hydrogen chloride. In practice, hydrogen chloride concentrations of about 0.1% are likely to be the highest attainable in the exit gas from a static bed reactor where the charge is fairly finely powdered, say minus 50 mesh (diameter of wire 0.009 inches, width of opening 0.011 inches—North American Standard).

The invention overcomes some of the above difficulties by the expedient of compacting the ferrous chloride into pellets or

briquettes, usually containing between 2 and 200 grams of ferrous chloride. Any hydrate of ferrous chloride up to the tetrahydrate may be used for this purpose. Anhydrous ferrous chloride is also suitable. Hydrated ferrous chloride crystals may also be used instead of pellets if they are of adequate size and uniformity.

Static beds of ferrous chloride pellets can be reduced with hot hydrogen up to any desired bed depth provided precautions are taken to avoid condensation of water vapour in the cooler parts of the bed.

The manufacture of pellets herein does not require any separate binder material and the pressures required are moderate. Usually a compaction pressure of 7,000 psi is used. Since no binder is needed the ferrous chloride and the product iron can be kept extremely pure. A suitable pellet profit is of disc-like form, but if a pellet-bed thickness exceeding about 12 inches is required, a more nearly spherical form of pellet is desirable. Other compacting techniques may also be used; for example, a ring-roll briquetting press has been found to be very suitable for the continuous production of large quantities of pillow-shaped briquettes of ferrous chloride.

One method of carrying out the reduction of ferrous chloride pellets is to circulate hydrogen, preheated to a temperature just below the melting point of ferrous chloride, through a large fixed bed of pellets, passing the gas therefrom through a conventional hydrogen chloride absorber and recycling the hydrogen through the heater and reactor. An alternative method is to reduce the ferrous chloride pellets in a continuous manner in some type of shaft kiln, employing a counter-current stream of hot hydrogen. Multiple tray kilns are also considered to be eminently suited to this process.

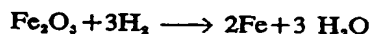
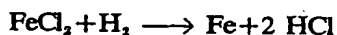
Increased thermal efficiency is obtained by carrying out the reaction with preheated hydrogen. The hydrogen is brought into the reactor at as high a temperature as is practicable. On the other hand if hydrogen at a temperature of, say 800°C, is directly applied to a ferrous chloride pellet, the pellet is likely to melt. The difficulty has been overcome by temperature-programming the course of the reduction so that an outer layer of iron sponge is formed on the ferrous chloride pellet at temperatures below the melting point. When this layer is sufficiently thick, the temperature can be raised to any preferred level so as to melt the remaining ferrous chloride. This molten chloride is soaked up by the previously formed iron sponge and is quickly reduced at the higher operating temperatures made possible by this technique.

The required temperature programme may be carried out with a static bed reactor by

increasing the temperature of the hydrogen fed into the reactor at the appropriate time. A preferred method of operation would be to use a continuous type of reactor in which the pellets are passed along from a low temperature reaction zone to a high temperature reaction zone.

Attention to pellet sizing and temperature control are necessary to exploit the full potential of this process without undesirable leakage of molten or vaporized ferrous chloride from the partly reduced pellets.

Reduction processes, as typified by the equations below, proceed in a manner essentially independent of each other provided the supply of hot hydrogen is adequate:



The time required for reduction under any given conditions is generally proportional to the linear dimensions of the particle in both the oxide and chloride cases. However, pellets or briquettes prepared from mixtures of oxide and chloride have been found to react at a rate governed by the overall pellet size so far as chloride reduction is concerned, but at a rate largely governed by individual grain size in the case of the oxide contained therein. The mixture of finely dispersed iron oxide ferrous chloride will serve to accelerate the reduction rate of the briquettes as a whole and has demonstrated a lower tendency to sticking of the briquette on the support or stickiness of the particles during reduction as is commonly encountered in fluidized bed reduction of ferrous chloride.

The presence of a fine oxide dispersion in pelletized or briquetted ferrous chloride is particularly advantageous in the technical production of iron via the chloride route since it enables the overall heat economy (in terms of iron units produced) to be considerably improved. This arises from the fact that the reduction equilibrium in the case of oxide reduction is much more favorable than that of chloride reduction, especially at relatively low temperatures 575°—400°C. It is in fact possible to design a continuous countercurrent reduction process in which preheated hydrogen is led into the system at, for example, 775°C under such conditions that essentially only chloride is reduced as the hydrogen temperature decreases to about 575°C, while oxide reduction predominates in the reaction zone corresponding to a further temperature drop from 575°C to 400°C. The heat remaining in the hydrogen is then available for any required dehydration of the ferrous chloride. The relatively cool hydrogen can then be further cooled and stripped of excess water and hy-

drogen chloride for economical recycling through the preheater and reduction furnace. In the reduction of ferrous chloride containing no oxide the hydrogen heat corresponding to the temperature drop from 575° to 400°C is largely wasted when high reduction rates are required.

The value of the invention is that, because of the lower heat of reduction of oxide as compared with chloride, it is possible in some reduction systems to achieve a three-fold increase in iron output for a given flow of hot hydrogen simply by blending the appropriate amount of oxide with the ferrous chloride prior to the pelletizing or briquetting stage. It should be noted that some increase in the pressure of the hot hydrogen may be desirable, in cases where the oxide content of the pellet or briquette is high, in the interests of improved heat transfer and rate of reaction through greater mass-action.

A further advantage of blending concentrates of oxidic ores with ferrous chloride prior to reduction accrues from the tendency of the metallic iron crystals to grow away from impurities under these conditions. It has, in fact, been found that small amounts of quartz (about 0.1%) present in the fine ore-concentrates used for blending with ferrous chloride are very readily removed from the reduced iron product by low-intensity magnetic separation in the dry state. The addition of pure ferrous chloride to the oxidic ore fines is also means of controlling the ratio of impurity to iron during the production of iron powder from ores.

It is important that the metal sponge produced be of satisfactory physical integrity. Indeed, this has been a severe limitation in hydrogen reduction techniques at less than melting temperature heretofore. By reason of the discovery of the ringing and metallic sound effects in the varieties of metal sponges produced in numerous experiments conducted by way of verification it was found that uniformity of an iron sponge could be improved by the use of a trace of calcium, sodium, sulphur or vanadium, zinc or nickel chlorides. It is suspected that the vapour pressure potential at the particular reducing temperature of an additive element contributes to distorting the grain boundaries of the crystalline form of the iron crystals during growth, that is to provide interlock and improvement of physical integrity of the iron sponge produced as set forth herein.

The invention is illustrated by the following Examples, Examples 1 to 4 of which are comparative and not part of the invention.

#### EXAMPLE 1

A 4.25 inch internal diameter reactor was charged with 3.25 pounds of 1 inch de-

ferrous  
chloride



hydrated ferrous chloride pellets, giving a bed depth of 7 inches. Water was circulated through an all glass hydrogen chloride absorber. The system was purged first with nitrogen, then with hydrogen. The hydrogen circulation rate was increased to 200 scfh (standard cubic feet per hour) and the heater was turned on. After 11 minutes the inlet hydrogen temperature was 450°C and acid mist was just visible at the absorber inlet. After 17 minutes more hydrogen began to trickle into the system through a low pressure regulator. The inlet hydrogen temperature was then 487°C. After 41 minutes the inlet and bed centre temperatures were 657°C and 577°C respectively, while the hydrogen consumption had reached 4.75 scfh. The pressure drop across the bed was 0.6 to 0.7 cm. water gauge. All conditions were held steady and after 83 minutes the specific gravity of the acid was 1.039. Thirty minutes later the gravity was 1.054 and the hydrogen consumption had dropped to 1.9 scfh. At this time, the temperature was increased. After a total time of 2 hours and 28 minutes, the inlet and bed centre temperatures were 742°C and 637°C respectively, while the hydrogen consumption fluctuated between 3.8 and 4.75 scfh. After 2 hours and 38 minutes the hydrogen consumption slowly decreased until 3 hours and 23 minutes from start-up the reaction ceased. The final specific gravity of the acid produced was 1.084, corresponding to about 16.8% hydrogen chloride. Figure 3 of the accompanying drawings illustrates the progress of the experiment. No residual ferrous chloride could be found in the iron product.

#### EXAMPLE 2

The reactor was charged with 10.0 lbs. of 1 inch ferrous chloride pellets having the approximate composition  $\text{FeCl}_2 \cdot 2.5 \text{H}_2\text{O}$ . The bed depth was 19 inches. The reactor was purged and heated as in Example 1. The absorber system contained only sufficient water to yield 20% hydrochloric acid when half of the charge reacted. The hydrogen inlet temperature was maintained at 650°C until the specific gravity of the recirculating acid was 1.040. During this time the hydrogen consumption reached a maximum of 3.8 scfh. The gas temperature was increased slowly during the remainder of the run until the inlet and bed centre temperatures were 790°C and 650°C respectively. Four hours after starting the reaction the specific gravity of the acid was 1.098, corresponding to 19.6% hydrogen chloride. During the next 2.5 hours the inlet and bed centre temperatures were further increased to 850°C and 750°C respectively. The maximum rate of hydrogen consumption observed was 7.6 scfh. During the second half of the reaction the recirculating acid was diluted with water

to maintain its strength between 20% and 24.2% hydrogen chloride. The total reaction time was 6.5 hours. The weight of iron produced was 3.3 lbs. and 1.75 gallons of 21.2% hydrochloric acid was recovered. The iron contained no residual ferrous chloride.

#### EXAMPLE 3

Nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) in the as received condition was dehydrated on a porous support in an air oven. The original weight was 221 g and the final weight was 145 g. In this form the chloride was substantially dehydrated and of the formula  $\text{NiCl}_2 \cdot (1.67\text{H}_2\text{O})$ . Further dehydration would only give rise to waste heat in the reduction cycle. The dehydrated nickel chloride was then pelletized in  $1\frac{1}{4}$ " diameter cylindrical form at 8,000 lb. per inch to provide pellets each weighing 14 g. The pellets were then reduced in hydrogen at the following rates of hydrogen gas flow and temperature to give the reported reduction times for complete reduction

345°C @ 40 cu ft/hr $\text{H}_2$	117 minutes
500°C @ 40 cu ft/hr. $\text{H}_2$	45 minutes

#### EXAMPLE 4

Cobalt Chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) was then dehydrated at 120°C in an air oven to obtain a substantially dehydrated form  $\text{CoCl}_2 \cdot (0.66 \text{H}_2\text{O})$ . This dehydrated form was amenable to pelletizing at 8,000 lb. per sq. inch to give  $1\frac{1}{4}$ " diameter cylindrical pellets, each weighing 14 g. To obtain a theoretically complete reduction at the same rate of hydrogen, however, as in the above examples, the following reduction temperatures gave the following reduction times:

548°C @ 40 cu ft/hr $\text{H}_2$	30 minutes
405°C @ 40 cu ft/hr. $\text{H}_2$	67 minutes

In these Examples, determination of complete reduction was obtained by measuring the amount of chloride in the reduced metal sponge. It is of special interest in this specification and according to the invention that the resulting iron sponge of Examples 1 and 2 while reasonably uniform did not conform in proportionate geometry exactly to the original geometry of the chloride and oxide pellet before reduction. When agitated, that is allowed to strike together in a glass bottle, the iron sponge samples had a dry sound of no particular distinctive or noticeable character. However, the nickel sponge produced had a distinctive ring when it was agitated of definite metallic character and quite noticeable. Further, the nickel sponge produced conformed in geometry proportionately to the geometry of the original pellet before reduction. The cobalt sponge, on the other hand, looked more like the iron sponge

and had a metallic sound when agitated, but not to the degree of the nickel sponge.

The above Examples show for comparison the treatment of substantially 100 per cent chloride. The following Examples show the presence oxides therewith and especially in the case of iron according to the invention.

#### EXAMPLE 5

Mixtures were made using ferrous chloride and ferric oxide. The ferrous chloride had a composition corresponding to  $\text{FeCl}_2 \cdot (1.6\text{H}_2\text{O})$  and passed through a 40 mesh screen. The ferric oxide was a super-concentrate of specular hematite, prepared by high intensity magnetic separation, and passed through a 150 mesh screen. The two materials were mixed in the amounts shown in Table 1.

TABLE 1

	Weight of $\text{FeCl}_2 \cdot 1.6\text{H}_2\text{O}$ (grams)	Weight of specular hematite (grams)
	14.0	nil
	14.0	1.4
	14.0	2.8
	14.0	5.6
	10.0	10.0
	5.6	14.0

The mixtures were pressed in a die at 8,000 psi to yield cylindrical pellets  $1\frac{1}{2}$ " diameter; the thickness of the pellets varied from about 0.4 to 0.5 inches. The pellets were reduced individually with hydrogen at a temperature of  $585^\circ\text{C}$ , the course of the chloride reduction being followed by continuous absorption and titration of the resulting hydrogen chloride. In all cases where chloride originally predominated in the mixture no effect by oxide on the reduction rate of chloride could be detected. When the pellets contained 50% or more oxide there was a slight initial retardation of chloride reduction probably arising from competition by the oxide for heat and hydrogen. In all cases reduction was complete within one hour and the resulting iron metal sponge was in all cases non-pyrophoric. By contrast, 14.0 grams of the hematite (without any chloride) placed in a shallow iron container  $1\frac{1}{2}$ " diameter was evidently fully reduced after one hour in hydrogen at  $585^\circ\text{C}$ , but was found to be pyrophoric after cooling and removal from the reduction apparatus.

The use of trace substances is disclosed in the following Examples:

#### EXAMPLE 6

Vanadyl chloride was added to the mixture of Example 5 prior to dehydration in an amount of .01 per cent by weight. Reduc-

tion was carried out at  $585^\circ\text{C}$  with hydrogen at a flow rate of 40 cu ft/hr. and was completed in 60 minutes. The trace amount of Vanadium resulted in the iron sponge having a clearly metallic ring and the geometry of the sponge conformed proportionately and uniformly to the original geometry of the pellet before reduction. The amount of Vanadium which was effective was quite adequate at .01 per cent and even lower amounts. Greater amounts contributed no noticeable improvement.

#### EXAMPLE 7

Nickel of 0.1 per cent by weight similarly employed as an additive in the manner of Example 6 demonstrated a definite improvement of structure but no ringing was discerned, nor a metallic sound detected. However, at .01 per cent by weight nickel had no effect at all and is not, therefore, necessarily considered as a desirable additive as contrasted with Calcium, Sodium, Sulphur or Vanadium. It is, however, useful and where occurring naturally or available in the substance to be reduced may be regarded as contributing to this invention.

#### EXAMPLE 8

Sulphur added in the same manner as in Example 6, but in the form of ferrous sulphate in solution added to a solution of ferrous chloride and then crystallized and dehydrated before mixture with the iron oxide was very effective in a range between .01 and 0.1 per cent by weight. The metal sponge produced had a metal spring-like sound, but not a definite ring. The sponge was of highly uniform appearance and regular consistent geometry proportionate to the pellet before reduction.

In the above examples an increase of reduction temperature would reduce the time of reduction. However, according to this invention a low temperature stage of reduction is first necessary in order to preserve the physical integrity of the pellet to provide a metallic skin thereon supporting same during a higher temperature stage of reduction where the reduction gas is at a temperature greater than, say the melting point of the chloride.

The invention will be understood in more detail by reference to the accompanying drawings wherein:

Figure 1 is a diagrammatic section of apparatus for use with the composition of matter and process of the invention.

Figure 2 is a flow sheet and diagrammatic outline of apparatus for a reduction cycle with the apparatus of Figure 1 permitting hydrogen regeneration and recovery according to the process herein.

Figure 3 is a plot of Example 1.

Figure 1 shows conveyor means 10 shown

in the form of the endless belt 11 extending about rolls 12 and 13. The belt 11 has gas passage openings 14 therein. Such belt may be in the form of a chain device or a series of spaced apart plates or plates with apertures therein. The specific form of the belt structure is not important so long as a movable conveyor or belt is provided which embodies gas passage openings therein, but which are so constituted and arranged as to carry on said support a bed 15 of pellets or particles of material to be reduced. Said conveyor means is arranged within an enclosure 16 having a gas inlet opening or fitting 17 adapted for the introduction of hot hydrogen near the delivery end 18 of the conveyor belt. The gas outlet from the enclosure 16 is provided by way of a column 19 leading to a gas outlet 20 for spent hydrogen. The column 19 is located in association with said conveyor or support remote from the delivery end 18, thus to define by virtue of the location of the inlet gas port 17 and the gas passages in the conveyor, three zones in the reducing apparatus of the invention in which the temperature is different.

In the final reduction zone the gas passing through the bed of material 15 on the belt 11 is subjected to hot hydrogen as indicated by arrows Y which flows therethrough and loses heat in so doing. Thus that zone in which the hot hydrogen first contacts the material being reduced may be described as that zone of final reduction at which the hydrogen is at maximum temperature. The zone of secondary contact of hydrogen with the particles or material being reduced may be identified as a low temperature reduction zone, designated as L. T. Reduction in Figure 1. The hydrogen in this zone of second contact with the material will be at a lower temperature and will be partially spent.

The zone of low temperature reduction is preferably such that the material being reduced is not caused to melt. Such a temperature may be defined in various ways depending upon the material being reduced. For example, ferrous chloride melts at about 675°C. The low temperature reduction, therefore, should be carried on according to this invention at less than this temperature. Nickel chloride has a much higher melting point. Again, the metal sponge produced by final reduction will have a melting point of the metal thereof substantially higher again. The purpose herein is to cause initial reduction at a reducing temperature lower than a temperature at which any of the material being reduced will melt and then to finalize or complete the reduction at as high a temperature as is practical, but not so high as to cause melting of the end metal product produced, although some degree of sintering thereof may be involved.

The temperature of hydrogen introduced should be in some cases as high as the melting point of the metal produced, but nevertheless should be low enough that at its secondary contact with the material being reduced in the low temperature reduction zone is less than that which would effect melting of any constituent particles of the mass being reduced.

In the case of the reduction of iron chloride the hot hydrogen may be introduced at a temperature of the order of 1000°C to attain a temperature of the hydrogen in the low temperature reduction zone of the order of less than 675°C. It will be observed that reducible material is stacked in the column 19 and that a gas from the low temperature reduction zone passes therethrough to the outlet 20. This is defined as a Dehydration zone within which metal chlorides are dehydrated by spent hydrogen resulting in the spent hydrogen being expelled at a temperature of the order of 200°C. As shown diagrammatically, the spent hydrogen is then recirculated through a HCl absorber 21 and the regenerated hydrogen is then heated by heater 22 and reintroduced to the inlet 17.

The introduction of material to be reduced and the delivery of reduced material from the apparatus in Figure 1 is preferably accomplished through a double gate gas seal type of arrangement. Thus in inlet end 23 of column 19 pellet feed is introduced into the hopper 24 having a bell valve 25 adapted to be opened to drop its contents into the intermediate hopper structure 26 having a bell valve 27 therefor and defining an intermediate chamber 28 adapted to be purged or pressurized with inert gas introduced through inlet 29. Again, at the outlet end 30 of the reducing apparatus the delivery end 18 of the conveyor support delivers the sponge metal particles 31 past the semi-hopper gate 32 into the cooling hopper 33 having gate 34. The region between the semi-hopper 32 and the cooling hopper 33 defines an open chamber 35 into which cold hydrogen is introduced by way of the inlet fitting 36. Upon release of gate 34 the reduced and cooled metal sponge is released into the delivery chamber 37 having a hopper 38 with gate 39 and which embodies an inlet fitting 40 for inert gas.

The use of inert gas at the outlet of the reduction apparatus is not necessary in the production of the product itself, but for the protection of personnel, unless some other means may be provided for the containment of hydrogen within the reduction system itself. Also, the introduction of inert gas at the feed end of the apparatus is utilized for the containment of hydrogen within the system and may be modified according to known equivalents to effect the same result.

The opening 41 of the column structure 19 may embody a gate (not shown) by means of which the depth of the bed of material to be reduced is determined. The baffle 42 serves as a deflector of the hydrogen gas stream to accomplish the flow according to the arrows Y substantially as shown thus to define the three zones described. It is known that the reduction does not proceed until dehydration is complete at any point of contact of hydrogen with a chloride hydrate particle.

In Figure 2 is disclosed a general process arrangement according to this invention in bold lines having associated therewith in lighter lines processing of material for reduction depending upon the manner in which the reduction process is to be employed.

Thus one may proceed with some suitable raw material, such as a mineral containing iron values, nickel or cobalt values and the like designated as raw material and subject same to leaching by hydrochloric acid in a dissolver. Metal chlorides are formed in the Dissolver and the solution is passed through a Filter and suitably evaporated to obtain a concentrated chloride solution from which it is desired to obtain metal chloride crystals. It is also contemplated that the raw material may itself be some kind of chloride solution, such as is obtained from waste pickle liquors, in which event the same would be merely filtered, concentrated, if desired, and then processed in a crystallizing apparatus to obtain a crystalline precipitate.

It is preferred that the kind of crystallizing apparatus used be of a form which can be adapted to serve as a hydrogen chloride absorber. There is shown a precipitator hydrogen chloride absorber which comprises a closed vessel into which metal chloride solution is fed and into which spent hydrogen containing hydrogen chloride is introduced and bubbled through the chloride solution thus to effect precipitation of metal chloride crystals therewith. The chloride crystals are withdrawn for drying in a dryer.

The regenerated hydrogen is passed to a heater from which it is directed to the reducer, the reducer being of the kind, for example, disclosed in Figure 1.

The metal chloride from the dryer is introduced to the reducer as a pellet fed in the manner described herein. Such metal chloride may have combined therewith in the case of iron especially oxides of iron in substantial quantities whereby the metal chloride content comprises at least 20% of the combined metal element content of metal chloride and oxide. Further and especially in the case of iron containing materials, trace additives may be introduced at this point as, for example, sulphur or vanadium. Where trace additives are added as crystals or other

salts or organic substances, it may be convenient to combine them with the metal chloride at some other point such as in the saturated chloride solution mother liquor in the precipitator hydrogen chloride absorber. Again, it is to be understood that the mixture of metal chlorides, oxides and/or trace additives will preferably be mixed in a suitable mixer and compacted into a useful pellet form for reduction in the reducer and introduced therein as a pellet feed.

#### WHAT WE CLAIM IS:—

1. A composition of matter convertible to a stable metallic form by hydrogen reduction at less than the melting temperature of the metal comprising a mixture of a compound of iron, cobalt or nickel with at least twenty per cent by weight of the metal content in the form of a chloride of the metal.

2. A composition according to claim 1 comprising a compound of iron and having in combination therewith of a trace amount of an element adapted to maintain the structural integrity of the mass when reduced by hydrogen to metallic form.

3. A composition according to Claim 2 in which the trace element is calcium, sodium, sulphur or vanadium.

4. A process of producing a stable metal product which comprises reducing a composition of matter according to any of the preceding claims with hydrogen at a temperature less than the melting point of the metal.

5. A process according to claim 4 in which prior to reduction the composition of matter is compacted under pressure to form pellets utilizing the chloride as a binder.

6. A process according to Claim 4 or Claim 5 in which the composition is continuously conveyed to a zone of final reduction, hot hydrogen is passed through in the zone of final reduction to complete the reduction thereof to metallic form, partially utilized hydrogen from the final reducing zone is recovered; the recovered hydrogen is used at less than the melting temperature of chloride content of the composition to effect partial reduction of the composition prior to delivery to the final reducing zone, the spent hydrogen from the partial reduction is recovered and the spent hydrogen is used for dehydration of chloride content of the composition prior to partial reduction.

7. A process according to Claim 6 in respect of iron or nickel compounds only which includes recovering the spent hydrogen which contains hydrogen chloride after dehydration of the composition therewith, contacting a metal chloride solution with the spent hydrogen and hydrogen chloride thereby to precipitate metal chloride crystals and to regenerate hydrogen, and recycling the

regenerated hydrogen with heat to the final reducing zone.

8. Apparatus for producing a stable metal product by reduction of a composition according to any of Claims 1 to 3 with hydrogen which comprises a dehydration column, perforate conveying means for receiving reducible material from the column and for conveying the composition at a predetermined depth to a point of delivery, an enclosure for conveying means, the column and the point of delivery, means for introducing hot hydrogen into the enclosure substantially at the point of delivery from the perforate conveyor, means associated with the conveyor for recovering hydrogen which has passed through material thereon and for redirecting the hydrogen through the conveyor to the column to define a low temperature reduction zone by the composition on the conveyor contacted by the redirected hydrogen, means for recovering spent hydrogen from upper regions of the column, and means for introducing material to the column to a sufficient depth therein above the conveyor to define a dehydration zone within which chloride content of the material is dehydrated by spent hydrogen prior to reduction.
9. Apparatus according to Claim 8 including means for regenerating spent hydro-

gen and heating it for re-introduction to the enclosure substantially at the point of delivery of the conveyor.

10. Apparatus according to Claim 8 or Claim 9 for the reduction of iron and nickel compounds only including a precipitator hydrogen chloride absorber containing a solution of a metal chloride, means for communicating spent hydrogen from the column to metal chloride solution in the absorber, means for conveying regenerated hydrogen from the absorber and communicating same with heat to substantially the delivery point of the conveyor, and means for collecting metal chloride precipitate from the absorber and introducing it to the column.

11. A process for producing a stable metal product substantially as hereinbefore described in any of Examples 5 to 8.

12. Apparatus for producing a stable metal product substantially as hereinbefore described with reference to Figures 1 and 2 of the accompanying drawings.

13. A composition of matter according to any of Claims 1 to 3 substantially as hereinbefore described.

ERIC POTTER & CLARKSON,  
Chartered Patent Agents,  
317 High Holborn,  
London, W.C.1.